

Compared reactivity of the OH-initiated tropospheric degradation of a series of methylated benzenes from benzene to hexamethylbenzene. A theoretical approach

Marie-Thérèse Rayez^{1,*}, Jean Claude Rayez¹ and E. Villenave²

1 University of Bordeaux, ISM (CNRS UMR 5255), 33405 Talence cedex, FRANCE

2 University of Bordeaux, EPOC-LPTC (CNRS UMR 5805), 33405 Talence cedex – FRANCE

* Corresponding author mt.rayez@ism.u-bordeaux1.fr

This study aims at a better understanding of the OH-initiated tropospheric degradation of aromatic hydrocarbons. Although this field of research has attracted a lot of attention in the last decades, there are still many open questions regarding important details of the reaction mechanism. In particular, in the case of substituted aromatics, there is increasing evidence in recent literature for the formation of ipso-type radical adducts (addition at ring position already occupied by a substituent): this possible reaction pathway has not been considered before in atmospheric chemistry models.

In this work, we used quantum chemistry methodology (DFT-M06-2X/6-31G(d,p)) coupled to kinetic calculations to put some light on the reaction of a series of methylated benzenes from benzene to hexamethylbenzene with OH radicals. We have considered all the possible addition pathways. One of the most important results that we have obtained is that ipso addition can be anticipated to be the predominant pathway in OH-addition reactions of some of the methylated benzenes.

A detailed analysis of the electronic properties has allowed us to interpret the results and build Structure Activity Relationships (SAR). A comparison with the few available experimental studies has been done.